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Transfer and degradation of the common pesticide  
atrazine through the unsaturated zone of the Chalk  
aquifer (Northern France)

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## Abstract

Groundwater in the Chalk aquifer is an important water resource whose quality has degraded due to fertilizer and pesticide use. Atrazine, classified as a priority substance, has been one of the most applied pesticides and also one of the most frequently detected pesticides in groundwater. The present study investigated the transfer and degradation of atrazine in the unsaturated zone of the Chalk aquifer in Northern France. The study was conducted in an underground quarry (Saint-Martin-le-Noeud), which provides a direct access to the water table and intercepts the unsaturated zone at different depths. The lake and the ceiling percolation of 16 sites throughout the quarry were followed. For 16 sites, the percolating flow rate and lake level were measured and the lake water was sampled for nitrate, atrazine and deethylatrazine (DEA, main degradation product of atrazine) analysis over 2.5 years. High spatial variations in hydrodynamics (percolating flow rate and lake level) and in lake water quality (atrazine between  $55 \pm 11$  and  $202 \pm 40$  ng  $L^{-1}$  and DEA between  $269 \pm 53$  and  $1727 \pm 345$  ng  $L^{-1}$ ) indicate that the properties of the unsaturated zone influence the transfer and the degradation of atrazine. A counterclockwise hysteresis characterizes

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the relationship between the lake level and atrazine concentration. Temporal variation shows that the atrazine is transferred through the matrix and fractures with a delay caused by the sorption process that differs in atrazine and DEA. The layer of clay-with-flints is shown to favor the degradation of atrazine near the surface. Preferential pathways may be created below clay-with-flints, through which the transfer of atrazine is quicker.

*Keywords:* Chalk groundwater; Atrazine; Unsaturated zone; Clay-with-flints

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## 1. Introduction

Chalk aquifer provides a large quantity of drinking water in Europe (Lapworth et al., 2015). The groundwater extracted from the Chalk aquifer of the Paris Basin supplies 70% of the drinking water consumed in the north of France (Lallahem, 2002). In the UK, the Chalk aquifer provides almost 60% of the total withdrawal groundwater (Azeez, 2017). It is also a substantial water resource to sustain and exchange with river flows (Grapes et al., 2005; Sear et al., 1999). Water quality of the Chalk aquifer is an important issue. Beginning in the 1970s, the impact of intensive agriculture on groundwater has been demonstrated (Headworth, 1989; Johnson et al., 2001). Numerous studies have shown degradation of groundwater quality of the Chalk aquifer due to the use of fertilizers and pesticides (Baran et al., 2008; Brouyère et al., 2004). To protect groundwater, it's crucial to better understand the transfer of pesticides from the soil to the water table, and particularly how pesticides move through the unsaturated zone (UZ), which has not been fully understood because of limited access. The Saint-Martin-le-Noeud underground quarry provides access to the UZ of the Chalk aquifer with groundwater at different depths (Barhoum et al., 2014). Chen et al. (2019) studied the transfer of water and contaminants through the matrix in the UZ of the quarry but the transfer of the pesticides to the water table remains unclear.

### 1.1. Pesticides - Atrazine

The World Health Organization defines pesticides as chemical organic compounds that are used to kill pests, fungi and unwanted plants (weeds). The European Drinking Water Directive sets the maximum limit of 0.1  $\mu\text{g/L}$  for each individual pesticide in drinking water and 0.5  $\mu\text{g/L}$  for total pesticides, i.e., the sum of all the substances detected in a sample. Among pesticide substances, atrazine is one of the most widely applied herbicides. It is classified as a priority substance due to its toxicity to the environment (Official Journal of the European Communities, 2001). Gammon et al. (2005) showed that life-time

30 exposure to atrazine may cause cancer. Araújo et al. (2018) demonstrated that  
 31 the presence of atrazine can affect the spatial distribution of fish in freshwater  
 32 by forming a chemical barrier isolating fish populations. Exposure to atrazine  
 33 can cause breaks in erythrocytes of *Carrasius auratus*, demonstrating the geno-  
 34 toxic potential of atrazine on fish (Cavas, 2011). In 2003, the application of  
 35 atrazine was banned in the European Union, although it is still widely used in  
 36 the United States (Mahler et al., 2017). It is still one of the most frequently  
 37 detected pesticides in freshwater (Vryzas et al., 2011).

38 Degradation is the process that transforms a substance into by-products.  
 39 The mechanisms of degradation are physical, chemical and biological (Coats,  
 40 1991). The main degradation products are deethylatrazine (DEA), deisopropy-  
 41 latrazine (DIA) and hydroxyatrazine (HA). DEA is the most frequently detected  
 42 degradation product of atrazine (Cahoon and Cutting, 2009). Biological pro-  
 43 cesses are responsible for metabolizing atrazine to DEA in soil by microorgan-  
 44 isms under aerobic conditions (Solomon et al., 2013). The half-life (the time  
 45 it takes for half of the pesticide to be degraded) of atrazine varies depending  
 46 on soil type, soil pH and the atrazine quantity applied. Accinelli et al. (2001)  
 47 showed that the average half-life of atrazine in non-sterile soils is 49 days under  
 48 aerobic conditions and 407 days under anaerobic conditions. The degradation of  
 49 atrazine mainly occurs in soil, but it may also occur in the UZ with the presence  
 50 of micro-organisms. Johnson et al. (2000) found no potential degradation in the  
 51 groundwater over a 200-day incubation. Issa and Wood (1999) showed that the  
 52 degradation of atrazine might occur in the UZ at a lower rate than in soil if  
 53 micro-organisms are present.

## 54 1.2. Chalk aquifer

55 Chalk is a marine sedimentary rock. It is a carbonate rock, made up of  
 56 more than 90% calcite and a variable proportion of dolomite (Fabricius, 2007).  
 57 The Chalk aquifer has been considered a double/triple porosity aquifer made of  
 58 matrix, fractures and conduits (in the most karstic areas). It is partly covered  
 59 by a layer of clay-with-flints (Laignel et al., 1999). The clay-with-flints is the

residual deposit formed from the dissolution, decalcification and cryoturbation of bedrock strata of the Chalk Group (Jukes-Browne, 1906). The thickness of the layer of clay-with-flints may reach several meters. Valdes et al. (2014) showed that the presence of clay-with-flints on the surface may have an impact on infiltration processes of water and solutes in the Chalk aquifer: it may store water on the surface and also create preferential pathways.

The conduits are developed in some areas of the Chalk aquifer, e.g., in Northern France. For the areas without conduits, the water transfer process may occur through the matrix and fractures. However, most studies considered that the main transfer process mainly occurs through the matrix (Cooper et al., 2006; Mathias et al., 2005). The water transfer through fractures may be active occasionally depending on different conditions such as rainfall intensity and soil moisture (Haria et al., 2003; Ireson and Butler, 2011). Van den Daele et al. (2007) showed that the solute exchange between the matrix porewater and the porewater in the fractures is driven by two possible processes: advection and diffusion. For an organic component such as atrazine, the sorption, i.e., adsorption - desorption, is a major process controlling their fate (Chefetz et al., 2004). Adsorption of an organic component on the Chalk delays the transport time, leading to a storage of the component in the Chalk UZ.

### 1.3. Pesticide study in the Chalk aquifer

For the past 30 years, most studies on pesticides have focused on soil components (Gutierrez and Baran, 2009) because it is widely considered that less than 1% of pesticides pass through soil components (Flury et al., 1995). Some studies observing pesticides (especially atrazine) in the groundwater show that the concentration can be higher than  $0.1 \mu\text{g L}^{-1}$ , and some even higher than  $0.5 \mu\text{g L}^{-1}$  (Vonberg et al., 2014; Lapworth and Gooddy, 2006). Thurman et al. (1992) observed the river-groundwater interaction with the exchange of pesticides and showed the importance of studying pesticides in groundwater because it may also impact surface water. Few studies took an interest in the transfer of atrazine in the UZ of the Chalk aquifer. Baran et al. (2008) studied the

infiltration processes of water with atrazine from 1989 to 2006, showing that the pesticide concentrations remained stable during periods of low-flow and increased episodically after rapid infiltration. Chilton et al. (2005) studied the main factors controlling the fate of pesticides in order to establish a model predicting pesticide behavior in the groundwater. However, these studies examined water samples from wells whose characteristics result from all the possible transfer processes in the Chalk aquifer, in both the unsaturated and saturated zones, in which it is difficult to focus on the transfer only through the UZ. Chen et al. (2019) showed that the transfer of atrazine in the UZ of the Chalk aquifer occurs mainly through the matrix with a velocity estimated between 0.7 and 2.1 m  $year^{-1}$  for the water percolating in the Saint-Martin-le-Noeud quarry (Northern France).

#### 1.4. Objective of the study

The aim of this study is to characterize the processes of the transfer and degradation of atrazine in the UZ of the Chalk aquifer. The study was conducted in the Saint-Martin-le-Noeud underground quarry in the Paris Basin (Northern France). Chen et al. (2019) have analyzed the ceiling percolation water in the same quarry. They have shown that the percolation water resulted mainly from the transfer through matrix. The quarry gives also a direct access to groundwater. Water table outcrops in the quarry, forming 16 lakes with different characteristics of UZ. The present study focus on the 16 underground lakes (water table). This study followed the spatio-temporal variation of the concentration of atrazine and its main degradation product DEA in groundwater has been followed. Spatio-temporal variations of the pesticides and nitrate are analyzed to characterize transfer processes in the unsaturated zone. Compared to nitrate variation, the variation of atrazine and DEA highlights the transfer process of pesticides including sorption effect.

## 117 2. Materials and methods

### 118 2.1. Site settings

119 Located in Saint-Martin-le-Noeud, 70 km north of Paris (Fig. 1), the under-  
120 ground quarry is 1200 m long and 150 m wide at an altitude of 165 m a.s.l. The  
121 coordinates of the quarry is 49.4 °N and 2.05 °E. The quarry was exploited  
122 from the 12th to the 18th century for chalk as a construction material, using  
123 room-and-pillar method. The quarry has been studied since 2012 (Barhoum  
124 et al., 2014; Chen et al., 2019).

125 The climate data used from January 2016 to April 2018 are recorded at the  
126 Beauvais station managed by Météo-France. The station is located 7 km from  
127 the quarry and is nearly at the same altitude. The average annual temperature  
128 is 11°C (minimum temperature in January and maximum temperature in July).  
129 The annual rainfall amount is 670 mm (values from Météo-France for the 1981-  
130 2010 period). An agricultural zone overlies the quarry. The landowner over  
131 the quarry provided information on agricultural practices beginning in 1974:  
132 cultivated fields contain corn, wheat and rapeseed. He claims that atrazine was  
133 used from 1977 to 2003.

#### 134 2.1.1. Geology and hydrogeology

135 The quarry has been excavated in the Upper Cretaceous chalk layer, within  
136 the limit of Coniacian and Turonian. The excavation followed the dip of Chalk  
137 layers. The dip is about 12° NNE. The Bray anticline is located at the western  
138 side of the quarry (Fig. 1). The Chalk aquifer, where the quarry is located, is  
139 considered to be an aquifer with two porosity types: matrix and fractures, since  
140 no karstic conduit was discovered. The quarry is partly covered by a layer of  
141 the clay-with-flints. The total porosity of the Chalk aquifer was estimated at  
142 40% (Lafrance, 2016).

143 Effective rainfall infiltrates through the unsaturated zone (chalk with or  
144 without clay-with-flints) before arriving into the quarry, where the water table  
145 outcrops at deeper parts. The water table forms 16 underground isolated lakes



in the quarry (Fig. 2). The infiltrated water flows into the lakes by two paths: percolating water dropping from the quarry ceiling and water circulating through the pillars and walls of the lake. The water of the lakes (corresponding to groundwater) is therefore a mixture of water coming from ceiling percolation and water passing through walls and pillars.

### 2.1.2. Characterization of the unsaturated zone of the study sites

The UZ thickness (from the soil surface to the quarry ceiling) varies spatially from 18 to 30 m. The thickness of the layer of clay-with-flints, measured with an electromagnetic ground conductivity geophysical instrument (EM31), varies from 30 cm to more than 5 m (Barhoum et al., 2014). Method EM31 measures the electrical conductivity of soil. Soil with clay-with-flints has higher electrical conductivity than soil without clay-with-flints. However, the relation between thickness of clay-with-flints and electrical conductivity of soil is not a linear relation. The exact thickness of clay-with-flints was measured for 3 sites: 30 cm for PED (lowest electrical conductivity,  $20 \text{ mS } m^{-1}$ ); 2 m for BLE (electrical conductivity medial,  $47.5 \text{ mS } m^{-1}$ ); more than 3 m for STA (highest electrical conductivity,  $72 \text{ mS } m^{-1}$ ).

According to Chen et al. (2019), the 16 sites (Fig.2) can be divided into three groups according to the UZ thickness and thickness of the clay-with-flints layer.

- Group 1 (G1): CAS, CHA, BLE, PIL, JAR and LIT. The sites have the highest UZ thickness (around 30 m) with a thin layer of clay-with-flints (electrical conductivity between 30 and  $60 \text{ mS } m^{-1}$ ).
- Group 2 (G2): NAT, TSA, STA, LUC, VOU, NIC and PI2. The sites have a high UZ thickness (around 28 m) with a thick layer of clay-with-flints (electrical conductivity higher than  $70 \text{ mS } m^{-1}$ ).
- Group 3 (G3): SQU, CAR and PED. The sites have the lowest UZ thickness (around 20 m) with a thin layer of clay-with-flints electrical conductivity less than  $30 \text{ mS } m^{-1}$ .

## 175 2.2. Data and methods

### 176 2.2.1. Sampling and measurements

177 Groundwater was sampled in 16 underground lakes (water table outcrops  
178 and porewater percolated through the UZ in quarry ceiling). From 2016 to  
179 2018, 14 campaigns were conducted: 2016-04-12, 2016-06-06, 2016-06-23, 2016-  
180 09-05, 2016-10-20, 2017-01-09, 2017-02-27, 2017-05-02, 2017-06-26, 2017-09-05,  
181 2017-10-23, 2018-01-16, 2018-04-10, 2018-05-16. The campaigns are divided into  
182 three groups. Table 1 presents the measurements and analysis done during each  
183 campaign.

184 For all 16 sites, the lake level and percolating volume were measured. For  
185 BLE, STA and PED, daily data of percolating flow rate and lake level were  
186 recorded from 2016-01-01 to 2018-05-16. Daily time series of the percolating  
187 flow rate were recorded using rain gauges. Daily time series of the lake level  
188 were recorded using CTD-Diver loggers.

189 The percolating flow was calculated as the ratio of the collected water depth  
190 (collected percolation volume divided by beaker area) between two field cam-  
191 paigns. In case of overflow, the percolating flow was underestimated. For each  
192 site, the lake level was standardized considering the lowest level as 0. Therefore,  
193 the standardized lake level of each campaign is the difference between the lake  
194 level measured and the lowest level.

### 195 2.2.2. Chemical analysis

196 Lake water from the 16 sites was sampled for nitrate, atrazine and DEA anal-  
197 ysis. The nitrate concentration was analyzed by ion chromatography (Dionex  
198 ISC 3000). The accuracy is  $1 \text{ mg } L^{-1}$  with 5% uncertainty. The ionic balance  
199 error was checked with other major ions ( $HCO_3^-$ ,  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Cl^-$ ;  
200  $SO_4^{2-}$ ). Atrazine, DEA, DIA and HA were analyzed using an on-line method  
201 with liquid chromatography-tandem mass spectrometry (Agilent Technology)  
202 with filtered samples (by  $0.2 \mu\text{m}$  filters) (Blanchoud et al., 2019). The quantifi-  
203 cation limit of this method is  $20 \text{ ng } L^{-1}$  with 20% uncertainty.

204 *2.2.3. Atrazine degradation rate*

205 Atrazine degradation rate can be expressed by DAR. DAR, introduced by  
206 Adams and Thurman (1991), is the ratio of the concentration of DEA, the main  
207 degradation product of atrazine to the concentration of atrazine, the primary  
208 molecule.

209 The equation to calculate DAR is:  $\text{DAR} = \text{DEA} / \text{Atrazine}$ .

210 This parameter is used as an indicator of atrazine degradation processes. A  
211 higher DAR value means greater degradation of atrazine.

### 212 3. Results

#### 213 3.1. Spatial variation

214 Figure 3 presents UZ thickness, the electrical conductivity of soil (indicator  
215 of the thickness of clay-with-flints), hydrodynamics (total percolation and stan-  
216 dardized lake level), quality (concentration of nitrate, atrazine and DEA) and  
217 DAR of the lake for the 16 sites. In Fig. 3, the six campaigns in group A (April  
218 2016 to September 2017, Table 1) were used for the boxplots, and all ten cam-  
219 paigns in groups A and B (Table 1) were used to calculate the total percolation  
220 between April 2016 and September 2017. Within 1200 m, high spatial variation  
221 was observed in the hydrodynamics and the quality of the groundwater.

222 Among the 16 sites, the total percolation varied from 180 cm to more than  
223 1500 cm during the same period covering nearly 1.5 years. The amplitude of lake  
224 level varied from 11 to 134 cm. LUC and VOU (G2) behaved very differently  
225 from the 14 other sites. These two sites had the highest total percolation (more  
226 than 1500 cm) but the smallest lake level amplitude (11 cm for LUC and 17 cm  
227 for VOU). Most of the sites had a lake level amplitude between 40 and 80 cm  
228 with a total percolation less than 1000 cm.

229 High spatial variation of nitrate concentration was observed. The medians  
230 of nitrate concentrations of the 16 sites varied between  $23 \pm 1$  and  $93 \pm 4$  mg  
231  $\text{NO}_3^- \text{L}^{-1}$ . The highest nitrate concentration observed was  $95 \pm 4$  mg  $\text{NO}_3^- \text{L}^{-1}$ .  
232 The concentrations observed in the quarry were at the upper end of what other  
233 studies had found. For example, El Gaouzi et al. (2013) observed a nitrate  
234 concentration between 34 and 49 mg  $\text{NO}_3^- \text{L}^{-1}$  in the Paris Basin. Sorensen  
235 et al. (2015) found nitrate concentrations varied between 30 and 60 mg  $\text{NO}_3^- \text{L}^{-1}$   
236 for the Chalk aquifer in the UK.

237 High spatial variation of atrazine and DEA concentration was observed.  
238 The concentration of DIA and HA is lower than the limit of quantification, so  
239 these two degradation products of atrazine are not presented in this study. The  
240 medians of the atrazine concentrations at the 16 sites varied between  $55 \pm 11$  and  
241  $202 \pm 40$  ng  $\text{L}^{-1}$ . The medians of the DEA concentrations of the 16 sites varied

242 between  $269 \pm 53$  and  $1727 \pm 345$  ng  $L^{-1}$ . The highest atrazine concentration was  
 243  $501 \pm 100$  ng  $L^{-1}$  and the highest DEA concentration was  $3941 \pm 788$  ng  $L^{-1}$ .  
 244 These atrazine and DEA concentrations were much higher than any published  
 245 values in other studies. For example, Baran et al. (2008) recorded that, from  
 246 2000 to 2006, for the Paris Basin, groundwater atrazine varied between 50 and  
 247 100 ng  $L^{-1}$  and DEA varied between 100 and 200 ng  $L^{-1}$ . Hakoun et al. (2017)  
 248 observed the maximum concentrations of atrazine and DEA less than 200 ng  
 249  $L^{-1}$  concentration of atrazine and DEA for the Chalk aquifer in Belgium.

250 High spatial variation of DAR was observed. The DAR medians for the  
 251 16 sites varied between 2.9 and 10.3, with the highest DAR value observed for  
 252 the lakes in the quarry at 41.9. These DAR values partly match what other  
 253 studies had found, e.g., maximum DAR around 3 for the groundwater of the  
 254 Luxembourg's Sandstone aquifer (Farlin et al., 2017). The high DAR values may  
 255 mean more degradation of atrazine in the soil, or also result from the different  
 256 transfer processes in DEA and atrazine.

257 Spatial variations were clearly observed between the three groups. For the  
 258 sites with thin layers of clay-with-flints (G1 and G3) the lake level amplitude  
 259 was between 46 and 134 cm. The G1 sites, with 30-m UZ thickness, had a low  
 260 concentration in nitrate (less than 40 mg  $NO_3^- L^{-1}$ , atrazine (less than 150 ng  
 261  $L^{-1}$ ) and DEA (less than 450 ng  $L^{-1}$ ). The G3 sites with a UZ thickness less  
 262 than 20 m showed higher concentrations in nitrate (medians up to  $93 \pm 4$  mg  
 263  $NO_3^- L^{-1}$ ), atrazine (medians up to  $202 \pm 40$  ng  $L^{-1}$ ) and DEA (medians up to  
 264  $1127 \pm 225$  ng  $L^{-1}$ ). The difference of nitrate, atrazine and DEA concentrations  
 265 between G1 and G3 could be due to the different UZ thicknesses of the sites.

266 For G2, the sites have a thick layer of clay-with-flints and an UZ thickness  
 267 around 28 m (about the same depth as for G1, thicker than G3). Water had  
 268 a DAR higher than the G1 and G3 sites. However, high spatial variation of  
 269 the quality of the groundwater was observed within G2. LUC and VOU were  
 270 particularly different from the 14 other sites. These two sites had the highest  
 271 concentrations of atrazine and DEA and the highest DAR, and also nitrate  
 272 concentration. The hydrodynamic features and water quality at LUC and VOU

could indicate that the transfer processes are different for these two sites.

### 3.2. Temporal variation

The boxplots in Fig.3 show a temporal variability of the hydrodynamics and quality of the lakes between the campaigns. The temporal variability differed between the sites and between the parameters. For example, the nitrate boxplots showed small variability between the campaigns for most of the sites. But for DAR, the temporal variability between the campaigns varied greatly between the sites: most of the sites showed very little variability while DAR at VOU varied between 5 and 30.

To understand the temporal variation in nitrate, atrazine, DEA and DAR, the data are presented over time (Fig.4). Four sites are presented: two sites with a thin layer of clay-with-flints (BLE in G1 and PED in G3) and two sites under a thick layer of clay-with-flints (STA and VOU in G2). Figure 4 presents the time series of the monthly rainfall amount, percolating flow rate, standardized lake level, nitrate, atrazine, DEA and DAR for the four sites (BLE, STA, VOU and PED) between 1 January 2016 and 16 May 2018.

The annual rainfall recorded at the Beauvais station was 750 mm for 2016 and 600 mm for 2017. The distribution of the rainfall varied from one year to the other. An intense rainfall event occurred in May 2016 with a monthly rainfall more than 170 mm. January 2018 was also a wet period with monthly rainfall greater than 100 mm. The temporal variation of the lake level and the percolating flow were, therefore, different between the two years. The lake level at VOU (Fig.4) presented little temporal variation, which is different from what was observed at the three other sites. BLE, STA and PED show a high temporal variation in lake level (e.g., lake level amplitude was 100 cm for BLE).

Temporal variation was observed for the lake level and the percolating flow rate at BLE, STA and PED: in 2016, the percolation stopped from November to December 2016, and percolation stopped earlier in 2017 from July to August. The highest percolating flow rate in 2016 was more than twice as high as in 2017. The lake level variation presented the same behavior as the percolating

303 flow rate. The maximum lake level variation in 2016 was also more than twice  
304 as high as in 2017. The temporal lake level and percolating flow rate variation  
305 between 2016 and 2017 may result from the temporal variation of rainfall.

306 The nitrate concentration shows a low variation for BLE, STA and PED,  
307 unlike hydrodynamics. Atrazine and DEA, on the other hand, show high tem-  
308 poral variation and little temporal variation for DAR. The differences between  
309 the temporal variation of nitrate and the temporal variation of atrazine and DEA  
310 mean that the transfer processes differ for the two molecules. For BLE, STA  
311 and PED, the temporal variation seems to be synchronized between atrazine  
312 and DEA but not synchronized with the lake level: the highest concentration of  
313 atrazine and DEA is delayed compared to the highest lake level and the lowest  
314 concentration of atrazine and DEA was observed at the same time as the lowest  
315 lake level (January 2018).

316 The temporal variation of the lake level and the percolating flow at VOU  
317 differed from BLE, STA and PED. The VOU lake level showed a little varia-  
318 tion. The percolating flow of VOU was uninterrupted but the intensity of the  
319 percolation varied over time. The fact that the temporal variation was observed  
320 for the percolating flow but not for the VOU lake level indicates that the VOU  
321 lake may be recharged continuously by other infiltrated water (water passing  
322 through walls and pillars).

323 High temporal variation was observed in atrazine, DEA and DAR for VOU.  
324 However, the temporal variations of atrazine differed from that of DEA. The  
325 highest concentration of atrazine was observed in January 2017 and the lowest  
326 concentration of atrazine was observed in January 2018, with the highest con-  
327 centration of DEA observed in April 2016. The differences between the temporal  
328 variation of atrazine and DEA indicate that the transfer processes of atrazine  
329 and of DEA are different for VOU. The DAR value at VOU showed a high  
330 temporal variation between 3 and 30. The highest DAR value was observed in  
331 January 2018 when the concentration of atrazine was at the lowest level.

## 332 4. Discussion

333 Since atrazine was used for the treatment of crops from 1977 to 2003, the high  
334 concentrations observed in atrazine and DEA indicate that the groundwater in  
335 the quarry has a residence time of one to several decades. Assuming a transfer  
336 within the UZ by piston flow, the apparent residence time between 14 and 40  
337 years can be calculated ( $2017 - 2003 = 14$  years and  $2017 - 1997 = 40$  years).  
338 With an UZ thickness between 18 and 31 m, the transfer velocity of atrazine and  
339 DEA for the groundwater in the quarry can be estimated between 0.45 and 2.21  
340 m/year. The apparent velocities match the matrix velocities (Van den Daele  
341 et al., 2007; Chen et al., 2019) but this cannot exclude the presence of transfer  
342 through fractures.

### 343 4.1. Degradation processes

344 In this study, most of the G1 and G3 sites had a DAR value around 3.5 with a  
345 very low temporal variation despite the high temporal variation observed in the  
346 concentration of atrazine and DEA. Farlin et al. (2017) also found DAR values  
347 around 3 for the groundwater of the Chalk aquifer. Several sites of G2, covered  
348 by a thick layer of clay-with-flints, had DAR values higher than 6. Martins et al.  
349 (2018) observed that atrazine could be easily adsorbed by clay-with-flints. Con-  
350 sidering that the clay-with-flints may be responsible for the storage of water and  
351 atrazine on the surface, atrazine at the G2 sites may stay longer on the surface,  
352 leading to more degradation. Degradation of atrazine is a biological process,  
353 normally under aerobic condition. The degradation of atrazine is considered  
354 occurring mainly in the soil with nearly no degradation in the UZ (anaerobic  
355 condition) (Johnson et al., 2000). Groundwater in the quarry is under aerobic  
356 condition. Therefore, degradation of atrazine may also occur in the quarry if  
357 micro-organisms are present (Issa and Wood, 1999; Solomon et al., 2013). The  
358 different DAR values in the groundwater related to the different thicknesses of  
359 the clay-with-flints layer indicate that the clay-with-flints on the surface may  
360 favor atrazine degradation processes with potential atrazine degradation in the  
361 groundwater if micro-organisms are present.



#### 362 4.2. Atrazine transfer process in the Chalk aquifer UZ

363 Chen et al. (2019) showed that the transfer process of atrazine is different  
364 from the transfer process of nitrate and estimated the transfer velocity of nitrate  
365 and atrazine in the Chalk UZ about  $1 \text{ m year}^{-1}$ . This shows that the transfer of  
366 the contaminants, nitrate and pesticide, is mainly driven by piston flow. With  
367 this hypothesis, the difference of the concentration of nitrate, atrazine and DEA  
368 between the sites of G1 and G3 may be due to the difference of the sites' depths.  
369 Deeper the groundwater is, less contaminant is presented.

370 Baran et al. (2008) observed that pesticides can be transferred through both  
371 matrix and fractures in UZ of the Chalk aquifer. A number of studies (Keim  
372 et al., 2012; Smith et al., 1970) suggested that transfer of water and contami-  
373 nants through fractures can account for 30% of the total recharge and, in certain  
374 conditions, transfer through fractures may dominate during the recharge period.  
375 Foster et al. (1991) showed that, unlike nitrate, pesticides are more likely trans-  
376 ferred through fractures. In this study, nitrate shows a small temporal variation,  
377 independent of water tables dynamic. This may lead to a conclusion that the  
378 transfer of nitrate occurs mainly through matrix by piston flow. Atrazine and  
379 DEA, on the contrary, show a high temporal variation, which seems to be linked  
380 to water tables dynamic. Therefore, the transfer of atrazine and DEA is differ-  
381 ent from the transfer of nitrate: other than matrix, it may occur mainly through  
382 fractures. In a recent study, Chen et al. (2019), who studied percolation water in  
383 the same quarry, considered percolation as water mainly passing through matrix  
384 with no atrazine and no DEA (concentration lower than Quantification limit,  
385  $20 \text{ ng L}^{-1}$ ) found in the percolation water of the G1 sites (water before 1977).  
386 In the present study, lake water at the G1 sites showed higher concentrations  
387 than percolation water (Fig.3) in atrazine (medians varied between  $67 \pm 13.4$   
388 and  $149 \pm 14.8 \text{ ng L}^{-1}$ ) and in DEA (medians varied between  $257 \pm 51.4$  and  
389  $514 \pm 102.8 \text{ ng L}^{-1}$ ). Therefore G1 lakes include some water infiltrated between  
390 1977 and 2003, younger than percolation water. The lakes are recharged by a  
391 transfer quicker than the transfer through matrix. Consequently, a significant  
392 proportion of the recharge is likely transfer through fractures.

393 Since atrazine and DEA are organic components, the transfer of these sub-  
394 stances in the Chalk aquifer UZ may be influenced by the sorption process  
395 (Wefer-Roehl et al., 2001). Ezra et al. (2006) showed that the transfer of or-  
396 ganic components in the Chalk UZ can be delayed due to adsorption. Nitrate, a  
397 soluble molecule, is less influenced by sorption, compared to the pesticides. In  
398 the present study, temporal variations were observed in atrazine and DEA but  
399 not in nitrate. These results indicate that the transfer processes are different be-  
400 tween nitrate and pesticides. Moreover, the maximum pesticide concentrations  
401 in the water table occurred a few weeks later than the maximum of the lake  
402 level (Fig.4). This could be explained by the sorption processes (adsorption and  
403 desorption). Atrazine and DEA adsorbed in the UZ are likely desorbed after  
404 the arrival of water recharging the water table. There is a 4-month delay due  
405 to the time for desorption.

#### 406 4.3. *Hysteresis (water level - pesticide concentration)*

407 To better understand the relationships between lake level and the concentra-  
408 tion of atrazine and DEA over time, Fig.5 was plotted to present the hysteresis  
409 between the water level and atrazine and DEA concentrations for four lakes  
410 (BLE, STA, VOU and PED). Data from April 2016 to May 2018 were used.  
411 Two types of hysteresis were observed (Fig.5a): i) no clear hysteresis for VOU,  
412 perhaps because the lake level does not present temporal variation; ii) counter-  
413 clockwise hysteresis clearly observed in atrazine and DEA for BLE, STA and  
414 PED. Atrazine and DEA showed similar hysteresis, meaning that the varia-  
415 tion of atrazine and the variation of DEA are synchronized. A sketch of the  
416 counterclockwise hysteresis is presented into four steps (Fig.5b).

- 417 (1) Start of the recharge: the concentrations of atrazine and DEA remain  
418 stable as the lake level starts to rise: not enough time for desorption.
- 419 (2) Recharge continues: concentrations of atrazine and DEA start to increase  
420 as the lake level continues to rise: there is enough time for the desorption.

- 421 (3) Decrease of recharge: concentrations of atrazine and DEA increase to the  
 422 maximum value as the lake level starts to drop: desorption continues.
- 423 (4) End of recharge: concentrations of atrazine and DEA decrease to the  
 424 minimum value as the lake level drops to the minimum: there is no more  
 425 desorption. All desorbed pesticides have been leached out and the con-  
 426 centration decreases to the lowest value.

427 The sites with temporal variation observed in lake level showed synchronized  
 428 transfers of atrazine and DEA. The transfer of the pesticides is delayed by the  
 429 adsorption and desorption processes.

#### 430 4.4. *Water table beneath clay-with-flints formation*

431 The LUC and VOU sites had a behavior different from the other 14 sites.  
 432 Both presented little temporal variation in terms of lake level but the highest  
 433 concentrations of atrazine and DEA. Valdes et al. (2014) suggested that the  
 434 layer of clay-with-flints may have two roles in the infiltration process: it can  
 435 store water near the surface and it can also accelerate the infiltration by creating  
 436 preferential pathways beneath it. The high concentrations of atrazine and DEA  
 437 observed in the LUC and VOU lakes may result from the quick transfer through  
 438 preferential pathways under the clay-with-flints. Below the layer of clay-with-  
 439 flints, a perched water table may form near the surface between the Chalk and  
 440 the clay-with-flints due to the contrast of hydraulic conductivity. The stored  
 441 water then infiltrates by the preferential pathways, recharging LUC and VOU  
 442 lakes continuously, explaining the low variation of lake levels and continuous  
 443 percolating flow of these two sites. The presence of preferential pathways may  
 444 allow micro-organisms entering the UZ, leading to the degradation of atrazine  
 445 in groundwater. LUC and VOU have higher DAR than other sites and this may  
 446 be because of higher degradation rate in soil or because of the degradation of  
 447 atrazine in the lakes with the presence of micro-organisms.

448 LUC and VOU also had the highest temporal variation of DAR. The high  
 449 temporal variation of DAR values may result from the differences observed be-

450 tween the atrazine concentration and the DEA concentration time series. This  
 451 difference between the temporal variation of atrazine concentration and DEA  
 452 concentration is due to the different transfer processes in atrazine and DEA.  
 453 Unlike other sites, VOU lake atrazine and DEA concentrations have different  
 454 temporal variations (Fig. 4). The VOU temporal variation of atrazine is similar  
 455 to other sites, so the transfer of atrazine is similar for all the sites, independent  
 456 of the thickness of the layer of clay-with-flints. However, the DEA of LUC and  
 457 VOU time series differ from the 14 other sites and no relation was observed  
 458 between the lake level and DEA for LUC and VOU. These results may be  
 459 explained by the different sorption capacities between atrazine and DEA. Sorp-  
 460 tion capacity depends on materials and the physico-chemical properties of the  
 461 organic component (Coquet, 2003). Bottoni et al. (1996) showed that atrazine  
 462 has lower mobility than DEA in soil with a Koc (Soil Organic Carbon-Water  
 463 Partitioning Coefficient) of  $111 \text{ mL } g^{-1}$  for atrazine and a Koc of  $38 \text{ mL } g^{-1}$  for  
 464 DEA (higher Koc indicates higher capacity of being adsorbed by soil). Brouwer  
 465 et al. (1990) and Mersie and Seybold (1996) showed that atrazine is more ad-  
 466 sorbed than DEA on soils, meaning that atrazine is more easily to be adsorbed  
 467 by the Chalk aquifer than DEA, and also more difficult to desorb than DEA.  
 468 Since we assumed that the transfer of atrazine and DEA for LUC and VOU  
 469 occurs mainly through preferential pathways, the transfer of DEA may occur  
 470 through fractures with very little adsorption in the Chalk aquifer. Atrazine is  
 471 more easily adsorbed, so its transfer is delayed by sorption. The preferential  
 472 pathways may result in different transfer processes of atrazine and DEA with  
 473 the transfer of DEA quicker because DEA desorbs more easily.

## 474 **5. Conclusion**

475 This study shows very high concentrations of atrazine and its degradation  
 476 product, DEA, in groundwater, which is the output of the UZ under an agricul-  
 477 tural area. The transfer velocities from soil surface towards the water table of  
 478 atrazine and DEA are estimated between 0.45 and 2.21 m/year. Spatial varia-

tions were observed in the groundwater concentration of nitrate, atrazine and DEA, and also in DAR in the groundwater, which may be related to the properties of the UZ of the Chalk aquifer (thickness of clay-with-flints and depth). Temporal variations were observed in the concentration of atrazine and DEA. The spatio-temporal variation of atrazine, DEA and DAR shows that:

- The transfer of atrazine and DEA occurs through both matrix and fractures, and the transfer is delayed by the sorption in the UZ.
- Clay-with-flints may favor the degradation of atrazine by creating a “perched water table”, leading to atrazine staying near the surface for a long time.
- Clay-with-flints can create preferential pathways, through which the transfers of atrazine and DEA are quicker. The transfers of atrazine and DEA differ in their preferential pathways because DEA is more easily to be desorbed.

The multi-sites with different UZ properties is a simple system (output of the UZ), which makes it possible to study how the UZ properties (UZ thickness and thickness of clay-with-flints) impact the transfer and degradation processes of pesticides. It is possible to apply this study to other studies on a larger scale, e.g., the study of the transfer of pesticides in the Chalk aquifer of the Paris Basin.

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## 506 References

- 507 Accinelli, C., Dinelli, G., Vicari, A., Catizone, P., 2001. Atrazine and metolachlor degradation  
508 in subsoils. *Biol. Fertil. Soils* 33, 495–500.
- 509 Adams, C., Thurman, E., 1991. Formation and transport of deethylatrazine in the soil and  
510 vadose zone. *J. Environ. Qual.* 20, 540–547.
- 511 Araújo, C.V.M., Silva, D.C.V.R., Gomes, L.E.T., Acayaba, R.D., Montagner, C.C., Moreira-  
512 Santos, M., Ribeiro, R., Pompêo, M.L.M., 2018. Habitat fragmentation caused by con-  
513 taminants: Atrazine as a chemical barrier isolating fish populations. *Chemosphere* 193,  
514 24–31.
- 515 Azeez, N.H., 2017. Hydrology of the Chalk Aquifer in East Yorkshire from Spring Recession  
516 Analysis. PhD Thesis. University of Leeds. England.
- 517 Baran, N., Lepiller, M., Mouvet, C., 2008. Agricultural diffuse pollution in a chalk aquifer  
518 (Trois Fontaines, France): Influence of pesticide properties and hydrodynamic constraints.  
519 *J. Hydrol.* 358, 56–69.
- 520 Barhoum, S., Valdes, D., Guerin, R., Marlin, C., Vitale, Q., Benmamar, J., Gombert, P., 2014.  
521 Spatial heterogeneity of high-resolution Chalk groundwater geochemistry Underground  
522 quarry at Saint Martin-le-Noeud, France. *J. Hydrol.* 519 (Part A), 756–768.
- 523 Blanchoud, H., Alliot, F., Chen, N., Valdes, D., 2019. Submitted: Rapid on-line solid phase  
524 extraction LC MS/MS analysis for atrazine, its by-products, simazine and S metolachlor  
525 in groundwater samples. *MethodesX* .
- 526 Bottoni, P., Keizer, J., Funari, E., 1996. Leaching indices of some major triazine metabolites.  
527 *Chemosphere* 32, 1401–1411. doi:10.1016/0045-6535(96)00049-5.
- 528 Brouwer, W.W.M., Boesten, J.J.T.I., Siegers, W.G., 1990. Adsorption of transformation  
529 products of atrazine by soil. *Weed Res.* 30, 123–128.
- 530 Brouyère, S., Dassargues, A., Hallet, V., 2004. Migration of contaminants through the un-  
531 saturated zone overlying the Hesbaye chalky aquifer in Belgium: a field investigation. *J.*  
532 *Contam. Hydrol.* 72, 135–164.
- 533 Cahoon, L.B., Cutting, R.H., 2009. Chapter 6 - forensic water quality investigations: Identifying  
534 pollution sources and polluters, in: Ahuja, S. (Ed.), *Handbook of Water Purity and*  
535 *Quality*. Academic Press, pp. 131–145.
- 536 Cavas, T., 2011. In vivo genotoxicity evaluation of atrazine and atrazinebased herbicide on fish  
537 *Carassius auratus* using the micronucleus test and the comet assay. *Food Chem. Toxicol.*  
538 49, 1431–1435.

539 Chefetz, B., Bilkis, Y.I., Polubesova, T., 2004. Sorption-desorption behavior of triazine and  
540 phenylurea herbicides in Kishon river sediments. *Water Res.* 38, 4383–4394.

541 Chen, N., Valdes, D., Marlin, C., Blanchoud, H., Guerin, R., Rouelle, M., Ribstein, P., 2019.  
542 Water, nitrate and atrazine transfer through the unsaturated zone of the Chalk aquifer in  
543 northern France. *Sci. Total Environ.* 652, 927–938.

544 Chilton, P.J., Stuart, M.E., Gooddy, D.C., Williams, R.J., Johnson, A.C., 2005. Pesticide  
545 fate and behaviour in the UK Chalk aquifer, and implications for groundwater quality. *Q. J. Eng. Geol. Hydrogeol.* 38, 65–81.

547 Coats, J.R., 1991. Pesticide Degradation Mechanisms and Environmental Activation, in:  
548 Pesticide Transformation Products. American Chemical Society. number 459 in ACS Sym-  
549 posium Series, pp. 10–30.

550 Cooper, J.D., Gardner, C.M.K., Mackenzie, N., 2006. Soil controls on recharge to aquifers.  
551 *Eur. J. Soil Sci.* 41, 613–630.

552 Coquet, Y., 2003. Sorption of Pesticides Atrazine, Isoproturon, and Metamitron in the Vadose  
553 Zone. *Vadose Zone J.* 2, 40–51.

554 Van den Daele, G.F.A., Barker, J.A., Connell, L.D., Atkinson, T.C., Darling, W.G., Cooper,  
555 J.D., 2007. Unsaturated flow and solute transport through the Chalk: Tracer test and dual  
556 permeability modelling. *J. Hydrol.* 342, 157–172.

557 El Gaouzi, F.Z.J., Sebilo, M., Ribstein, P., Plagnes, V., Boeckx, P., Xue, D., Derenne, S.,  
558 Zakeossian, M., 2013. Using  $^{15}\text{N}$  and  $^{18}\text{O}$  values to identify sources of nitrate in karstic  
559 springs in the Paris basin France. *Appl. Geochem.* 35, 230–243.

560 Official Journal of the European Communities, E.U., 2001. Decision no.2455/2001/EC of the  
561 european parliament and of the council of 20 november 2001 establishing the list of priority  
562 substances in the field of water policy and amending directive 2000/60/EC.

563 Ezra, S., Feinstein, S., Yakirevich, A., Adar, E., Bilkis, I., 2006. Retardation of organo-  
564 bromides in a fractured chalk aquitard. *J. Contam. Hydrol.* 86, 195–214.

565 Fabricius, I.L., 2007. Chalk: composition, diagenesis and physical properties. *B. Geol. Soc. Denmark* 55, 97–128.

567 Farlin, J., Bayerle, M., Pittois, D., Gall, T., 2017. Estimating pesticide attenuation from  
568 water dating and the ratio of metabolite to parent compound. *Ground Water* 55, 550–557.

569 Flury, M., Leuenberger, J., Studer, B., Fluhler, H., 1995. Transport of Anions and Herbicides  
570 in a Loamy and a Sandy Field Soil. *Water Resour. Res.* 31, 823–835.

571 Foster, S.S.D., Chilton, P.J., Stuart, M.E., 1991. Mechanisms of Groundwater Pollution by  
572 Pesticides. *Water Environ. J.* 5, 186–193.

573 Gammon, D.W., Aldous, C.N., Carr, W.C., Sanborn, J.R., Pfeifer, K.F., 2005. A risk assess-  
574 ment of atrazine use in California: human health and ecological aspects. *Pest Manag. Sci.*  
575 61, 331–355.

576 Grapes, T.R., Bradley, C., Petts, G.E., 2005. Dynamics of riveraquifer interactions along a  
577 chalk stream: the River Lambourn, UK. *Hydrol. Process* 19, 2035–2053.

578 Gutierrez, A., Baran, N., 2009. Long-term transfer of diffuse pollution at catchment scale:  
579 Respective roles of soil, and the unsaturated and saturated zones (Brévilles, France). *J.*  
580 *Hydrol.* 369, 381–391.

581 Hakoun, V., Orban, P., Dassargues, A., Brouyère, S., 2017. Factors controlling spatial and  
582 temporal patterns of multiple pesticide compounds in groundwater (Hesbaye chalk aquifer,  
583 Belgium). *Environ. Pollut.* 223, 185–199.

584 Haria, A.H., Hodnett, M.G., Johnson, A.C., 2003. Mechanisms of groundwater recharge and  
585 pesticide penetration to a chalk aquifer in southern England. *J. Hydrol.* 275, 122–137.

586 Headworth, H.G., 1989. Contamination of Groundwaters from Diffuse Sources arising from  
587 Farming Activities. *Water Environ. J.* 3, 517–521.

588 Ireson, A.M., Butler, A.P., 2011. Controls on preferential recharge to Chalk aquifers. *J.*  
589 *Hydrol.* 398, 109–123.

590 Issa, S., Wood, M., 1999. Degradation of atrazine and isoproturon in the unsaturated zone:  
591 a study from Southern England. *Pestic. Sci.* 55, 539–545.

592 Johnson, A.C., Besien, T.J., Bhardwaj, C.L., Dixon, A., Goody, D.C., Haria, A.H., White,  
593 C., 2001. Penetration of herbicides to groundwater in an unconfined chalk aquifer following  
594 normal soil applications. *J. Contam. Hydrol.* 53, 101–117.

595 Johnson, A.C., White, C., Lal Bhardwaj, C., 2000. Potential for isoproturon, atrazine and  
596 mecoprop to be degraded within a chalk aquifer system. *J. Contam. Hydrol.* 44, 1–18.

597 Jukes-Browne, A.J., 1906. The Clay-with-Flints; its Origin and Distribution. *Q. J. Geol. Soc.*  
598 62, 132–164.

599 Keim, D.M., West, L.J., Odling, N.E., 2012. Convergent Flow in Unsaturated Fractured  
600 Chalk. *Vadose Zone J.* 11.

601 Lafrance, N., 2016. Étude des effets de leau sur les phnomnes de rupture et de deformation  
602 affectant les carrières souterraines de craie. PhD Thesis. Université de Lorraine. France.



603 Laignel, B., Quesnel, F., Meyer, R., Bourdillon, C., 1999. Reconstruction of the Upper  
604 Cretaceous chalks removed by dissolution during the Cenozoic in the western Paris Basin.  
605 *Int. J. Earth Sci.* 88, 467–474.

606 Lallahem, S., 2002. Structure et modélisation hydrodynamique des eaux souterraines : appli-  
607 cation à l’aquifère crayeux de la bordure nord du Bassin de Paris. PhD Thesis. Université  
608 Lille 1. France.

609 Lapworth, D.J., Baran, N., Stuart, M.E., Manamsa, K., Talbot, J., 2015. Persistent and  
610 emerging micro-organic contaminants in Chalk groundwater of England and France. *Env-*  
611 *iron. Pollut.* 203, 214–225.

612 Lapworth, D.J., Gooddy, D.C., 2006. Source and persistence of pesticides in a semi-confined  
613 chalk aquifer of southeast England. *Environ. Pollut.* 144, 1031–1044.

614 Mahler, B.J., Van Metre, P.C., Burley, T.E., Loftin, K.A., Meyer, M.T., Nowell, L.H., 2017.  
615 Similarities and differences in occurrence and temporal fluctuations in glyphosate and  
616 atrazine in small midwestern streams USA during the 2013 growing season. *Sci. Total*  
617 *Environ.* 579, 149–158.

618 Martins, E.C., de Freitas Melo, V., Bohone, J.B., Abate, G., 2018. Sorption and desorption  
619 of atrazine on soils: The effect of different soil fractions. *Geoderma* 322, 131–139.

620 Mathias, S.A., Butler, A.P., McIntyre, N., Wheeler, H.S., 2005. The significance of flow in  
621 the matrix of the Chalk unsaturated zone. *J. Hydrol.* 310, 62–77.

622 Mersie, W., Seybold, C., 1996. Adsorption and Desorption of Atrazine, Deethylatrazine,  
623 Deisopropylatrazine, and Hydroxyatrazine on Levy Wetland Soil. *J. Agric. Food Chem.* 44,  
624 1925–1929. URL: <https://doi.org/10.1021/jf950370k>, doi:10.1021/jf950370k.

625 Sear, D.A., Armitage, P.D., Dawson, F.H., 1999. Groundwater dominated rivers. *Hydrol.*  
626 *Process* 13, 255–276.

627 Smith, D.B., Wearn, P.L., Richards, H.J., Rowe, P.C., 1970. Water Movement in the Un-  
628 saturated Zone of High and Low Permeability Strata by Measuring Natural Tritium, in:  
629 *Isotope hydrology 1970*, Vienne.

630 Solomon, R.D.J., Kumar, A., Satheesa Santhi, V., 2013. Atrazine biodegradation efficiency,  
631 metabolite detection, and trzD gene expression by enrichment bacterial cultures from agri-  
632 cultural soil. *J. Zhejiang Univ. Sci. B* 14, 1162–1172.

633 Sorensen, J.P.R., Butcher, A.S., Stuart, M.E., Townsend, B.R., 2015. Nitrate fluctuations  
634 at the water table: implications for recharge processes and solute transport in the Chalk  
635 aquifer. *Hydrol. Process.* 29, 3355–3367.

- 636 Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., Kolpin, D.W., 1992. A  
637 reconnaissance study of herbicides and their metabolites in surface water of the midwestern  
638 United States using immunoassay and gas chromatography/mass spectrometry. *Environ.*  
639 *Sci. Technol.* 26, 2440–2447.
- 640 Valdes, D., Dupont, J.P., Laignel, B., Slimani, S., Delbart, C., 2014. Infiltration processes in  
641 karstic chalk investigated through a spatial analysis of the geochemical properties of the  
642 groundwater: The effect of the superficial layer of clay-with-flints. *J. Hydrol.* 519 (Part A),  
643 23–33.
- 644 Vonberg, D., Vanderborght, J., Cremer, N., Putz, T., Herbst, M., Vereecken, H., 2014. 20  
645 years of long-term atrazine monitoring in a shallow aquifer in western Germany. *Water*  
646 *Res.* 50, 294–306.
- 647 Vryzas, Z., Alexoudis, C., Vassiliou, G., Galanis, K., Papadopoulou-Mourkidou, E., 2011.  
648 Determination and aquatic risk assessment of pesticide residues in riparian drainage canals  
649 in northeastern Greece. *Ecotoxicol. Environ. Saf.* 74, 174–181.
- 650 Wefer-Roehl, A., Graber, E.R., Borisover, M.D., Adar, E., Nativ, R., Ronen, Z., 2001. Sorp-  
651 tion of organic contaminants in a fractured chalk formation. *Chemosphere* 44, 1121–1130.

Table 1: The measurements and analyses made for each campaign.

Groups	Campaigns	Sites	Measurements	Analyses
A	2016-04-12, 2016-06-23,	16 sites	percolating flow rate, lake level	nitrate, atrazine, DEA
	2016-10-20, 2017-01-09,			
	2017-02-27, 2017-09-05			
B	2016-06-06, 2016-09-05,	16 sites	percolating flow rate, lake level	N.A.
	2017-05-02, 2017-06-26			
C	2017-10-23, 2018-01-16,	BLE, STA,	percolating flow rate, lake level	nitrate, atrazine, DEA
	2018-04-10, 2018-05-16	VOU, PED		

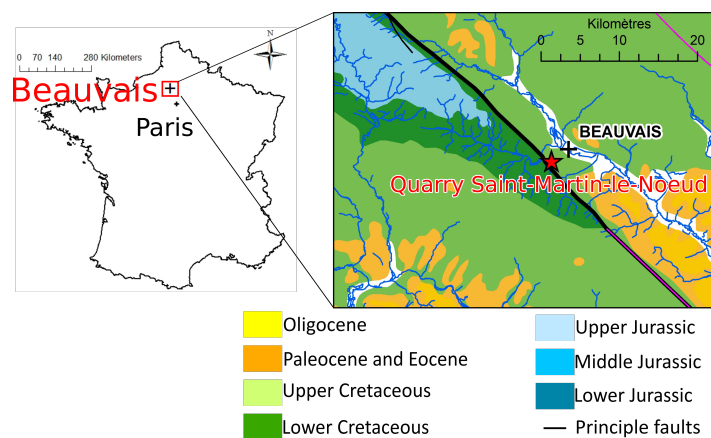


Figure 1: Location of the study site with the zoom of the geology of the study site.

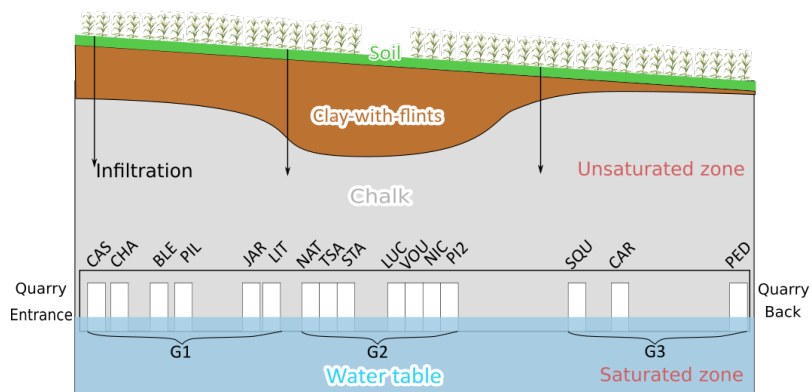


Figure 2: Schematic cross section of the Saint-Martin-le-Noeud quarry with the presentation of the 16 sites in the quarry.

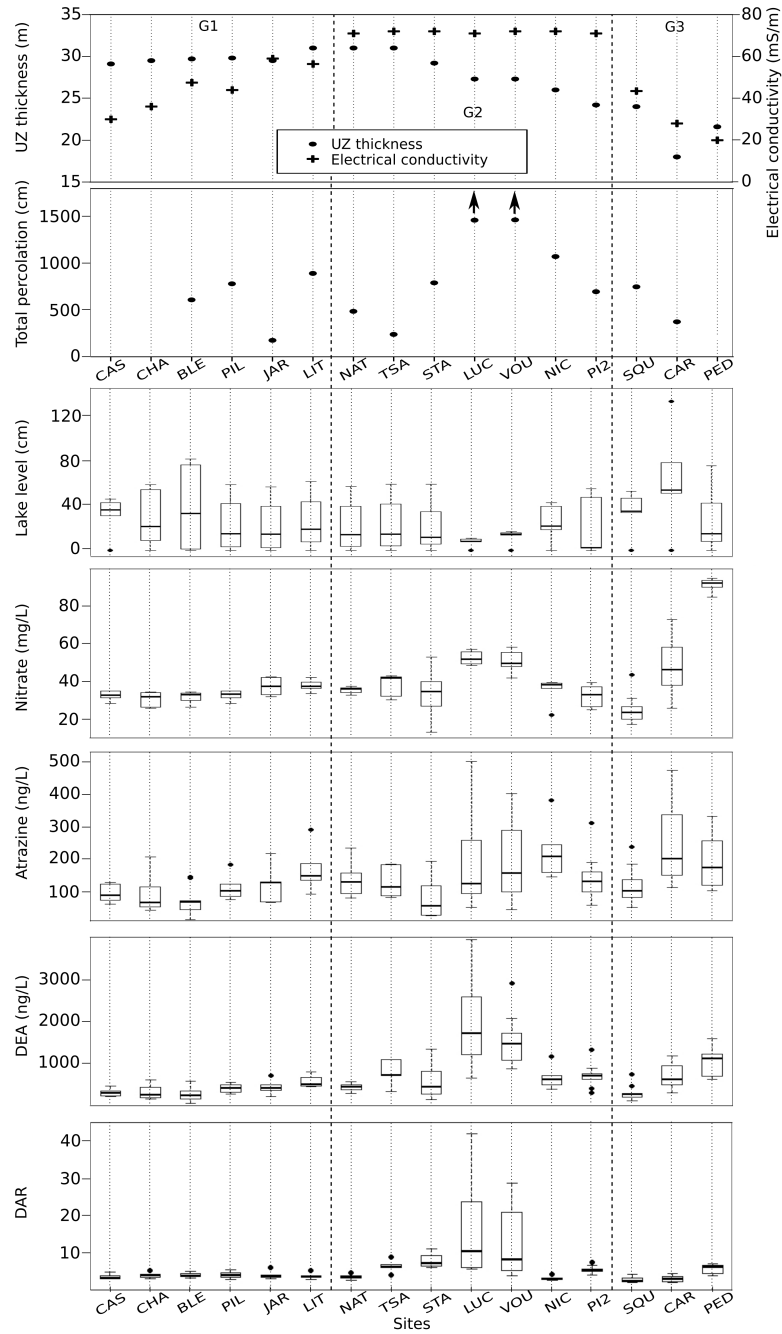


Figure 3: UZ thickness and electrical conductivity of the 16 sites. The total percolation between April 2016 and September 2017 and the boxplot of lake level variation, of concentration of nitrate, atrazine and DEA, and of DAR of the lake of the 16 sites. Campaigns used for the box are: 2016-04-12, 2016-06-23, 2016-10-20, 2017-01-09, 2017-02-27, 2017-09-05. The box range between the 25th and 75th percentiles, whiskers correspond to minimum and maximum, horizontal bars indicate the median. The 16 sites are divided into three groups: G1, G2 and G3.

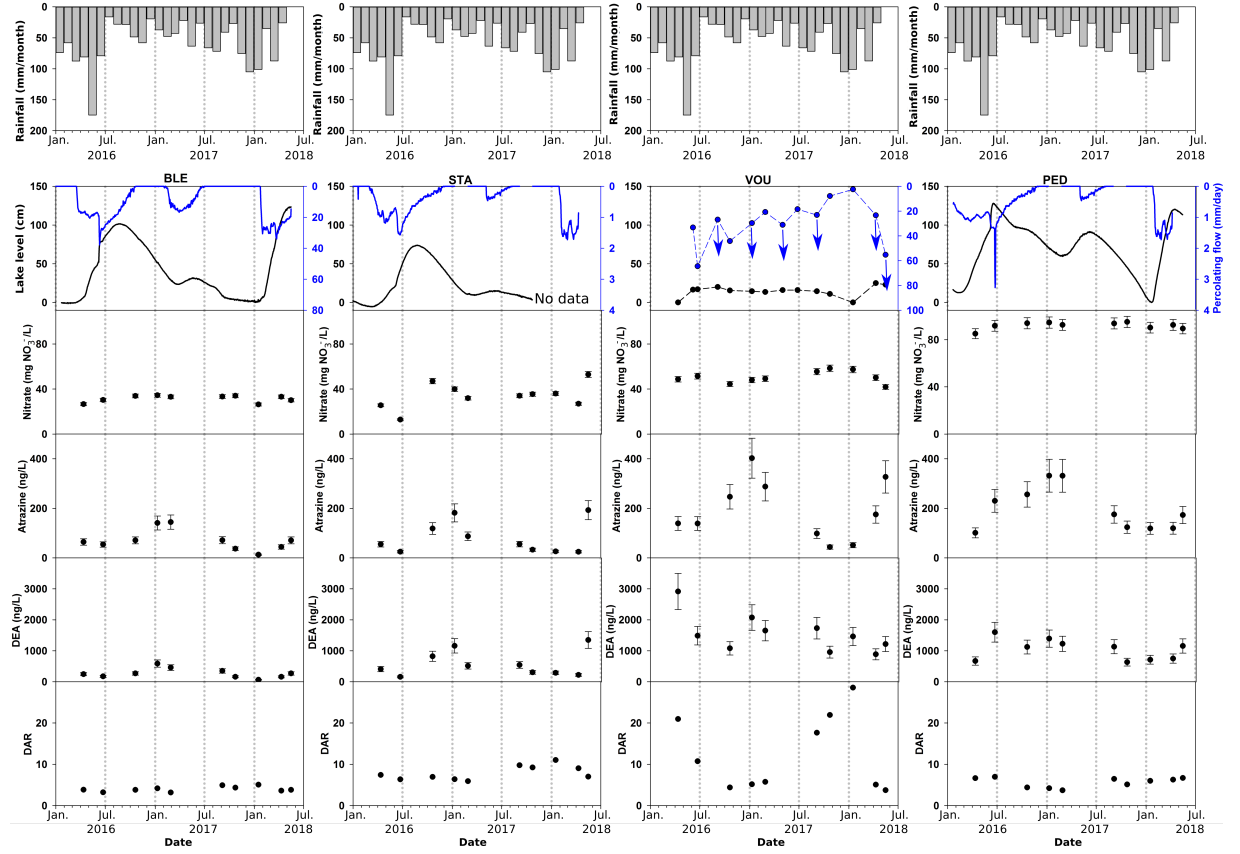


Figure 4: Time series of rainfall, lake level variation, percolating flow, nitrate, atrazine, DEA and DAR from 2016-01-01 to 2018-06-31 for BLE, STA, VOU and PED. Time series of percolating flow is presented with reversed y-axis. Arrows of the percolating flow of VOU indicate that the values are underestimated.

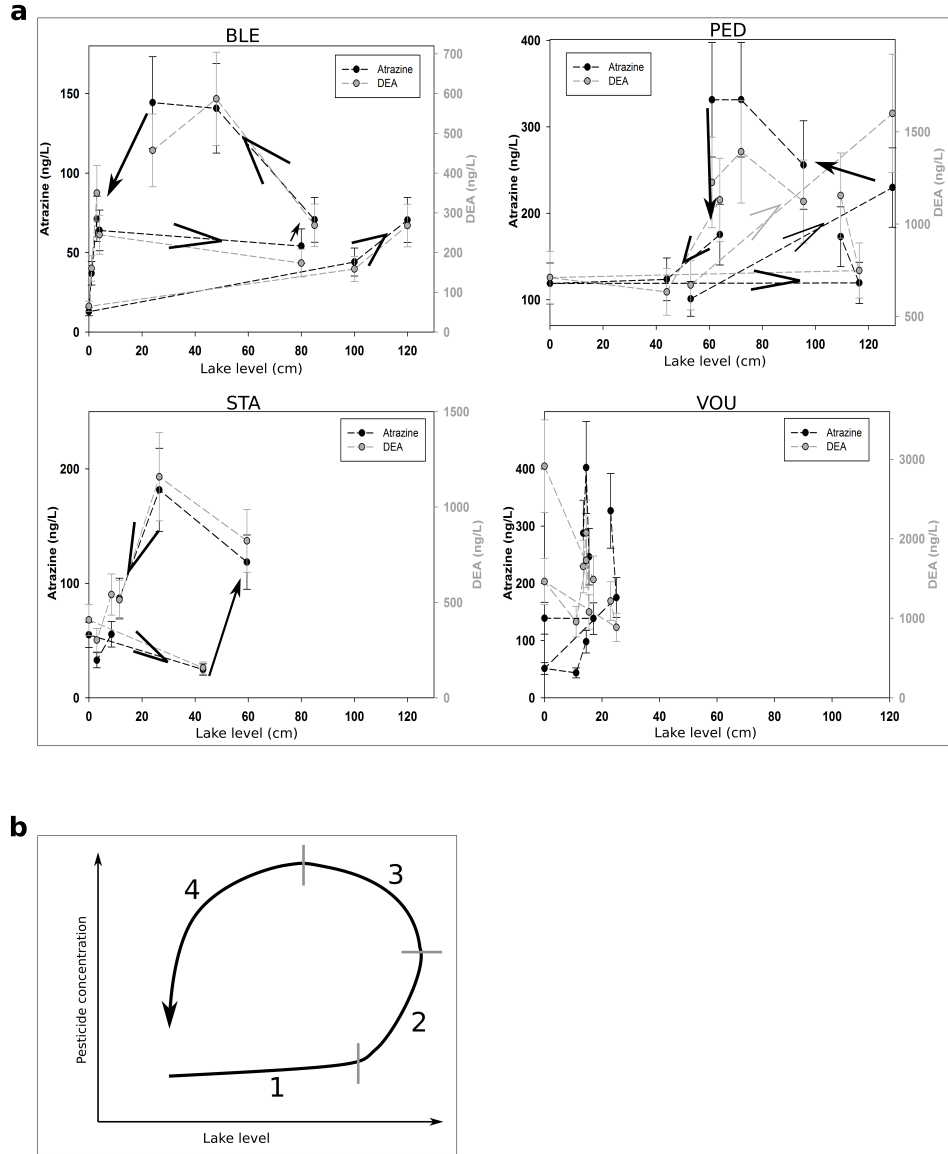


Figure 5: Hysteresis between lake level and pesticide concentration. a, hysteresis between atrazine, DEA and lake level variation for BLE, STA, Vou and PED. Campaigns used are: 2016-04-12, 2016-06-23, 2016-10-20, 2017-01-09, 2017-02-27, 2017-09-05, 2017-10-23, 2018-01-16, 2018-04-10, 2018-05-16. b, Sketch of the hysteresis observed between lake level variation and pesticide concentration.

